Longitudinal static optical properties of hydrogen chains: Finite field extrapolations of matrix product state calculations

Sebastian Wouters[1], Peter A. Limacher[2], Dimitri Van Neck[1] and Paul W. Ayers[2]

[1]Center For Molecular Modeling, Ghent University, Ghent, Belgium
[2]Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

Journal of Chemical Physics 136, 134110 (2012). [doi:10.1063/1.3700087] [arXiv:1202.0177v2]

1. Introduction

- Matrix product states (MPS) are the *natural* variational ansatzes for 1D non-critical systems.

$$|\Psi\rangle = \sum_{\{i_1 \ldots i_L\}} \sum_{\{k_1 \ldots k_{L-1}\}} M^{i_1}_{k_1} M^{i_2}_{k_1 k_2} \ldots M^{i_L}_{k_{L-1}} |i_1 \ldots i_L\rangle$$

  They can capture all relevant entanglement, at a much lower cost than exact diagonalization (ED).
- Chemists are interested in the non-linear optical (NLO) properties of quasi-1D systems.
- MPS calculations of NLO properties allow to
  1. Assess approximative methods
  2. Extrapolate highly accurate (quasi-ED accuracy) thermodynamic limit (TDL) data

2. Quantum chemistry vs. condensed matter

- The theory of quantum chemistry is known. In the non-relativistic regime & for quasi-instantaneous electron motion (Born-Oppenheimer approximation):

$$\hat{H} = -\frac{1}{2}\sum_{i \in \text{el.}} \vec{\nabla}_i^2 - \sum_{i \in \text{el.}; A \in \text{nucl.}} \frac{Z_A}{|\vec{R}_A - \vec{r}_i|} + \sum_{i<j \in \text{el.}} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

- To allow implementation on a computer, a finite basis set has to be chosen as orbital degrees of freedom. The Hamiltonian can then be written in 2nd quantization as:

$$\hat{H} = \sum_{i,j \in \text{orb.}} T_{ij} \sum_{\sigma} \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} + \frac{1}{2} \sum_{i,j,k,l \in \text{orb.}} V_{ijkl} \sum_{\sigma\tau} \hat{a}^\dagger_{i\sigma} \hat{a}^\dagger_{j\tau} \hat{a}_{l\tau} \hat{a}_{k\sigma}$$

- Due to the general two-body interaction, it is hard to keep track of all matrix elements (in contrast to condensed matter systems). Several tricks exist though.

3. SU(2) $\otimes$ U(1) invariant MPS

- Spin and particle number are conserved for chemical systems under influence of an electric field.
- Global symmetry can be imposed on the MPS by requiring that each M-tensor is an irreducible tensor operator of the imposed symmetry groups:

$$M^i_{k_L k_R} = M^{(ss^z N)}_{(j_L j_L^z N_L \alpha_L)(j_R j_R^z N_R \alpha_R)} = \langle j_L j_L^z s s^z \mid j_R j_R^z \rangle \, \delta_{N_L + N, N_R} \, T^{(sN)}_{(j_L N_L \alpha_L)(j_R N_R \alpha_R)}$$

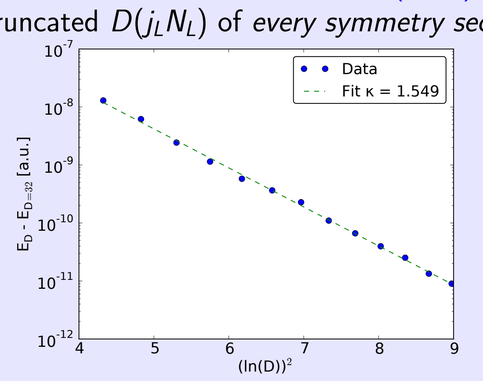
  S. Singh et al., Phys. Rev. A 82, 050301 (2010).
  The Wigner-Eckart (WE) theorem can be used to work with reduced MPS tensors.
- Because both $\hat{a}^\dagger_m$ and $(-1)^{\frac{1}{2}-m}\hat{a}_m$ transform as irreducible tensor operators of SU(2) $\otimes$ U(1), partial contractions of Hamiltonian terms can be stored in reduced form too. Our code hence contains no spin projections.
- Advantages of symmetry:
  1. Only the relevant part of the Hilbert space is scanned
  2. Tensors acquire a sparse block structure
  3. The WE theorem allows to work with reduced tensors
  4. Virtual dimension requirements become smaller
  5. Less sweeps are needed

4. Convergence

- $D(j_L N_L) = \text{size}(\alpha_L)$ corresponds to a virtual dimension of $(2j_L + 1)D(j_L N_L)$ in a non-symmetry adapted MPS.
- The MPS ground state energy follows

$$\ln(E_D - E_{exact}) = a - \kappa(\ln(D))^2$$

  with D the total virtual dimension.
  G. Chan et al., J. Chem. Phys. 116, 4462 (2002).
  We have truncated $D(j_L N_L)$ of *every symmetry sector* to D:



- For all applications in the paper, D is chosen large enough for the MPS results to be indistinguishable from ED.

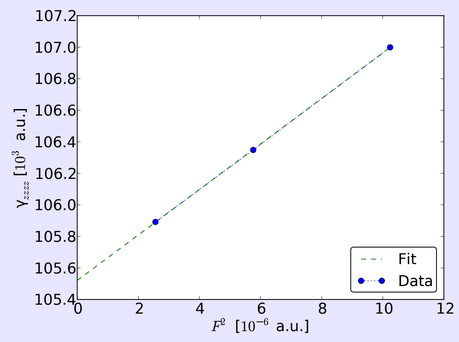
5. Finite field extrapolations

- E.g. the longitudinal static 2nd hyperpolarizability γ_{zzzz}.
- For centrosymmetric systems, its value can be obtained with the following minimal finite difference formula:

$$\gamma_{zzzz} = \left(\frac{-6E(0) + 8E(F) - 2E(2F)}{F^4} \right)_{F \to 0}$$

  where $E(F)$ is the energy when an electric field F is applied in the longitudinal direction.
- Values for F have to be chosen with care:
  1. Too small values enhance energy errors.
  2. Too large values cause higher order effects.
- The error on γ_{zzzz} for finite values of F is of $\mathcal{O}(F^2)$. This effect can eliminated with the extrapolation

$$\gamma_{zzzz}(F) = \gamma_{zzzz}(0) + cF^2$$



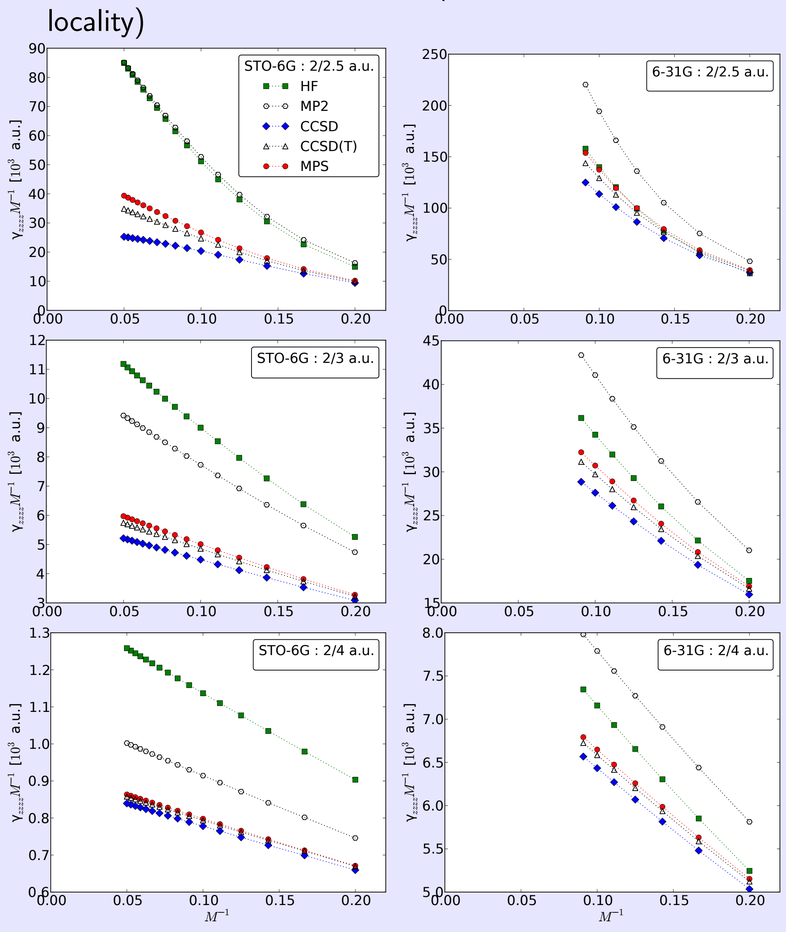
6. The raw data

We used

- 3 H-chain configurations: $R_f = 2$ a.u. and R varies

$$\text{H} \overset{R_f}{} \text{H} \overset{R}{\cdots\cdots} \text{H} \overset{R_f}{} \text{H} \overset{R}{\cdots\cdots} \text{H} \overset{R_f}{} \text{H} \overset{R}{\cdots\cdots} \text{H} \overset{R_f}{} \text{H}$$

- Different chain lengths: H_{2M} (M H_2 molecules)
- 5 levels of theory: HF, MP2, CCSD, CCSD(T) & MPS
- 2 basis sets: STO-6G & 6-31G (Löwdin transformed for locality)

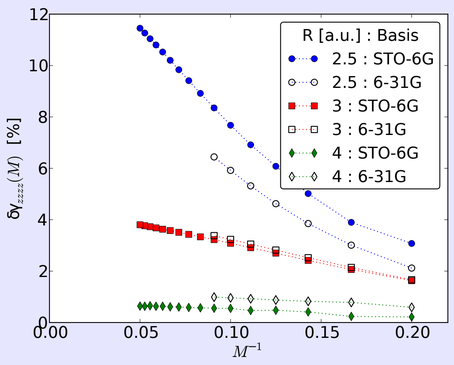


- γ^{HF}_{zzzz} has no fixed relative position. The other methods have.
- Adding electron correlation approximately does not lead to a smooth transition from mean-field theory to MPS($\approx$ED).
- CCSD(T) results are consistently the closest to MPS($\approx$ED).

7. CCSD(T) accuracy

- Look at the relative deviation

$$\delta\gamma_{zzzz}(M) = \frac{\gamma^{MPS}_{zzzz}(M) - \gamma^{CCSD(T)}_{zzzz}(M)}{\gamma^{CCSD(T)}_{zzzz}(M)}$$

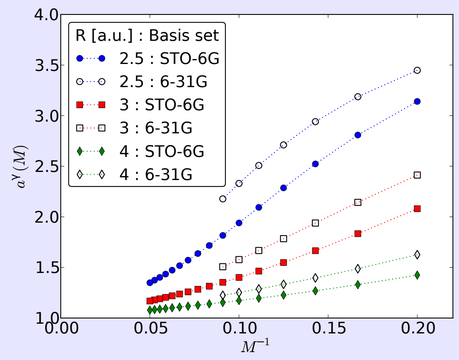


- Large $R \to$ well separated H_2 molecules
- Small $R \to$ delocalized electrons
- When going from large to small R (small to large electron delocalization), CCSD(T) begins to fail as it cannot describe the correlation of a large number of electrons correctly. CCSD(T), the current reference for NLO properties, can hence be inadequate.

8. TDL data extrapolation

- $\gamma \propto M^{a(M)}$ is often proposed.
- $a(M)$ depends on M. For small M, the possibility for optical excitations opens and $a(M)$ is large. For large M, the chain can fully contain optical excitations and $a(M)$ tends to 1.
- Estimate the exponent:

$$a^\gamma(M) = \frac{\ln(\gamma^{MPS}_{zzzz}(M)) - \ln(\gamma^{MPS}_{zzzz}(M-1))}{\ln(M) - \ln(M-1)}$$

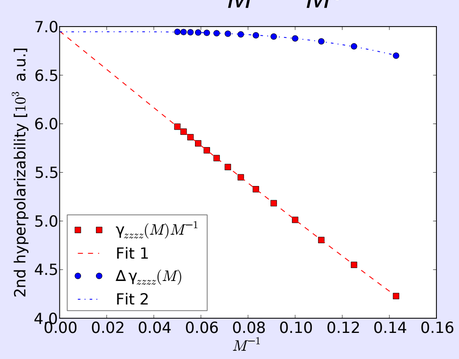


- If $a(M) \approx 1$, it's reasonable to assume:

$$\frac{\gamma^{MPS}_{zzzz}(M)}{M} = a_0 + \frac{a_1}{M} + \frac{a_2}{M^2} + \frac{a_3}{M^3}$$

- From this equation:

$$\Delta\gamma^{MPS}_{zzzz}(M) = \gamma^{MPS}_{zzzz}(M) - \gamma^{MPS}_{zzzz}(M-1) = a_0 + \frac{b_2}{M^2} + \frac{b_3}{M^3} + \mathcal{O}(M^{-4})$$



- By using both, the extrapolation accuracy can be assessed.

9. Extrapolated MPS data

Quantity	Basis set	R [a.u.]	$q(M)/M$	$\Delta q(M)$
α_{zz} [a.u.]	STO-6G	2.5	17.41	17.41
		3.0	9.464	9.462
		4.0	5.733	5.733
	6-31G	2.5	39.00	39.20
		3.0	21.27	21.27
		4.0	13.55	13.55
γ_{zzzz} [10^3 a.u.]	STO-6G	2.5	52.64	52.74
		3.0	6.953	6.945
		4.0	0.9303	0.9301
	6-31G	2.5	410.8[(a)]	424.0[(a)]
		3.0	48.52	48.45
		4.0	8.275	8.269

(a) $a^\gamma(M)$ is still rather large

10. Conclusions

- Adding electron correlation approximately does not lead to a smooth transition from mean-field theory to MPS($\approx$ED).
- CCSD(T) results are consistently the closest to MPS($\approx$ED).
- CCSD(T) however gives inadequate results for excitations involving a large number of electrons, e.g. the second hyperpolarizability when the electron delocalization is large.
- Static NLO TDL data with ED accuracy can be extrapolated from MPS calculations, as long as the chain length exceeds the typical length scale of an optical excitation.

Acknowledgements

- Research Foundation Flanders (S.W.)
- Swiss National Science Foundation (P.A.L.)
- NSERC (P.W.A.)
- Stevin Supercomputer Infrastructure at Ghent University
- Sharcnet $\in$ Compute Canada national HPC platform